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(54) **WAVEGUIDE SENSOR**

WELLENLEITERSENSOR

CAPTEUR A GUIDE D'ONDE

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(56) References cited:

WO-A-86/07149

GB-A- 2 185 308

US-A- 4 929 049

US-A- 5 026 139

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Description

[0001] The invention relates generally to chemical sensors using optical waveguides and more particularly to refractive index type chemical sensors using optical waveguides.

[0002] Optical waveguides, structures which guide light by total internal reflection, have been used in chemical sensors. Most waveguide chemical sensors are fiber optic chemical sensors (FOCS) based on optical fibers which guide light through the core by total internal reflection at the core/clad interface using a clad of lower refractive index than the core.

[0003] U.S. Patent 4,929,049 describes a fiber optic refractive index sensor using a thin film metal clad which allows modulation of transmitted signal by changes in the refractive index of the surrounding medium.

[0004] U.S. Patent 4,913,519 to Klainer, et al., describes an optical sensor for detection of ice formation or other chemical species in which a striped clad is formed on a fiber optic core or other waveguide structure. The spaced stripes of clad material have a refractive index less than the light guiding means and substantially equal to the refractive index of the chemical species to be detected. When the species is not present, the gaps between the clad strips allow light leakage so that little or no light is transmitted through the waveguide. When the species is present, it fills the gaps to form a complete clad which totally internally reflects light within the waveguide so that light is transmitted there-through.

[0005] P.C.T. Patent Application PCT/CH86/00072 to Tiefenthaler, et al., describes an optical waveguide sensor to selectively determine the presence of substances and the variations of refractive index in measured substances. The sensor is formed of a planar waveguide film, or a narrow strip, with a diffraction grating formed thereon. The thin film waveguide is formed of an oxide or polymer. The grating provides input or output coupling or acts as a Bragg reflector within the waveguide. The sample interacts with the waveguide in the region around the grating. In order to selectively establish the presence of specific substances, a layer of selective chemisorption material is formed on the thin film waveguide. The remainder of the waveguide surface may be covered by a low-index protective layer. According to Tiefenthaler the presence of a chemisorbed layer and/or the modification of the refractive index of the measurement substance modifies the refractive index within the waveguide film, which produces measurable changes in the propagation of light waves therein.

[0006] The invention provides a waveguide sensor in accordance with claim 1, and other aspects of the invention in accordance with other independent claims.

[0007] The larger surface area of the planar waveguide makes it much easier to apply the desired coatings, particularly where clad materials of specific crystallographic orientation are utilized. The improved coatings provide a sensor which can operate at high temperature with a long lifetime which is highly desirable for in-situ long-term monitoring applications. The ability to form patterned planar coatings also facilitates the production of waveguide sensors which use combinations of clad materials of different specificities to detect a chemical species of interest.

[0008] Different clad materials have different specificities to various chemical species. The specificity of different clads can be used to make simultaneous or multiple measurements which yield a better result by subtracting out the effects of other substances. Single waveguides can be clad with a plurality of different species-specific clad segments. Alternatively, multiple waveguide sensors each with a different species-specific clad could be used in combination. The clad segments are chosen with various specificities so that information about the particular analyte of interest can be calculated from the detected signals from each sensor or from the plurality of clad segments on a single waveguide sensor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] In the accompanying drawings:

Figure 1 is a perspective view of a planar waveguide having a clad formed thereon.

Figure 2 is a perspective view of a planar waveguide having a clad formed thereon including a clad segment which introduces controlled light leakage.

Figures 3A and 3B are side views illustrating light transmission in the waveguides of Figures 1 and 2, respectively. Figure 3C is a top plan view of the clad segment of the waveguide of Figure 2 showing clad porosity and absorption of sample molecules on the clad.

Figure 4 is a top plan view of a planar waveguide showing various configurations and orientations of clad segments.

Figure 5 is a graph of light output intensity as a function of light leakage.

Figure 6A is a schematic view of a measurement system using a planar waveguide with a species-specific clad segment.

Figures 6B-F are various embodiments of measurement systems utilizing planar waveguides with two or more species-specific clad segments.

Figure 7 is a side view of a planar waveguide measurement system including means for blocking light which propagates straight down the waveguides.

Figure 8 is a side view of a waveguide with a clad segment formed of two layers of different materials.

5 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] A waveguide sensor will now be described with at least one clad segment wherein the index of refraction of the waveguide clad segment and waveguide body have been selected relative to the index of the species of interest to produce a controlled leakage of light from the waveguide through the clad segment when the species of interest contacts the clad segment. The transmission properties of the waveguide thus vary as the refractive index of the species of interest present in the surrounding medium (in liquid or vapor or water emulsion form), and thus provide a measure of the refractive index. The clad segments are also chosen for their specificity to particular species of interest so that the sensor response identifies the species.

[0011] The waveguide body and clad segment materials are selected with indexes N_1 , N_3 to optimize the effect of the refractive index of the chemical species of interest. Both selective affinity and refractive index must be considered to get required specificity and sensitivity. In a mixture it is the average refractive index which is measured, i.e. the refractive index is one number which is determined by all the species present and their concentrations. Sorting, or enhancing the response of a particular species or group of compounds, is thus a prerequisite to a refractive index measurement.

[0012] The proper matching of the refractive indexes N_1 , N_2 , N_3 , N_4 in configuring the waveguide sensor produces an optimized sensor tailored to a particular species. The species of interest has a refractive index N_4 . The clad segment is formed of a material with index N_3 which has a known affinity for the particular chemical species. When the species of interest contacts the clad segment on the waveguide, a refractive index N^* is produced which is a function of both N_3 and N_4 . The choice of the clad segment material, as well as various characteristics of the clad segment such as thickness and porosity, in combination with the chemical species of interest thus produce the refractive index N^* seen by the waveguide sensor in the interaction region. For the waveguide to leak light, the index N^* must be greater than N_1 so a suitable material for the waveguide can be selected. Once the waveguide material is selected, the remaining clad material with index N_2 can be selected. The index N_2 must be less than N_1 and is preferably at least about 10% less so that the critical angle is relatively large and a significant amount of the input light signal will be totally internally reflected down the waveguide. The index N_2 and the position of the clad segment(s) should also be selected so that a significant portion of the totally internally reflected light beam is incident on the clad segment(s).

[0013] As shown in Figure 1 an optical waveguide 10 is formed of a planar optical waveguide body 12 having a refractive index N_1 and a clad 14 having a refractive index N_2 less than N_1 formed thereon. The waveguide body 12 forms the light guiding means through which the light is guided, similar to the core of an optical fiber. The optical waveguide operates by total internal reflection of light at the waveguide body 12/clad 14 interface since the index N_2 is less than N_1 for all light within an angle determined by the ratio N_2/N_1 . (Only details of the sensing surface containing clad 14 are shown, although the opposed surface would be mounted on a suitable substrate or be coated with a suitable coating to produce total internal reflection within the waveguide 12.) The waveguide 12 also has a pair of end surfaces 16 for inputting and outputting a light signal.

[0014] As shown in Figure 2, the clad 14 on waveguide body 12 contains a clad segment 18 of different refractive index N_3 . With reference to Figure 2, the chemical species of interest has an index N_4 . The material of clad segment 18 is chosen so that it is specific to a species of interest and has an index N_3 which in combination with the index N_4 of the species of interest when present in the surrounding medium and the index N_1 of the waveguide produces a controlled light leakage from which the presence of the species of interest can be determined.

[0015] The operation of the waveguides of Figures 1 and 2 to transmit light are illustrated in Figures 3A and 3B, respectively. In Figure 3A the light is input through one end face 16 of waveguide 12 and is totally internally reflected at the interface between waveguide 12 and clad 14 until it is output through the other end face 16. (As previously described, total internal reflection also occurs on the opposed surface of waveguide 12 from clad 14 by suitable means.) End faces 16 are preferably at angles as shown to eliminate light reflection on entrance and exit from the waveguide. In Figure 3B, clad 14 continues to produce total internal reflection of the light within the waveguide 12 but clad segment 18 allows a controlled amount of the light to leak from the waveguide, thereby reducing the light output signal from the waveguide. Light leakage is controlled by the selection of the index N_1 of the waveguide and index N_3 of the clad segment so that in combination with the index N_4 of the species of interest, the effect is optimized.

[0016] As illustrated in Figure 3C, the light transmissivity or leakage is controlled by the clad segment 18 which is shown as having pores (cells) 19 into which atoms or molecules 17 of the species of interest are absorbed. The combination of the clad 18 and absorbed species 17 produces a localized refractive index which is used to control light leakage.

[0017] As illustrated in Figure 4, the clad segments 18a, b, c, d, e can take a variety of shapes and orientations including stripes in any direction on the surface or square or circular areas. The ease of producing patterned coatings

on a planar waveguide surface, using conventional technology such as photoresist, masking, and etching from the semiconductor field, provides great flexibility in making clad segments which maximize contact with the sample.

[0018] The light intensity of the signal transmitted through the waveguide, thus will vary as a function of the presence of the chemical species of interest which causes a light loss during the transmission. The result of changes in the output signal are illustrated in Figure 5. The dynamic range of the sensor is designed to provide easy measurement of the species in the concentration range of interest, i.e. the sensor is designed to produce a large signal change for a selected range of species concentration. By appropriate choice of the sensor parameters, the light loss that occurs over a measurement range of interest is a significant percentage of the total light signal (no loss) so that the signal difference can be easily measured. Choice of light intensity and wavelength also can be used to obtain the desired dynamic range.

[0019] A simple sensor system 29 utilizing the waveguide sensor is illustrated in Figure 6A. The waveguide 26 having a clad segment 28 formed thereon is placed between a source 22 and detector 24. Suitable optics 23, 25 such as lenses, filters, polarizers, etc. may be utilized between the source and detector and the waveguide, if necessary. The signal from detector 24 is input into processing means 27 such as a digital computer to record, display, and otherwise process the signals. Although clad segment 28 is shown as a stripe oriented along the axis between the source and detector, other orientations or shapes of the clad segment could be used. When the surrounding medium which contacts the clad segment 28 on the surface of waveguide 26 contains a species of interest for which the waveguide 26/clad segment 28 have been designed, light leakage occurs so that the detected light intensity of the signal propagated through the waveguide decreases. Light sources including lasers (e.g., diode lasers), lamps, or LEDs can be used. The detector may be a photodiode.

[0020] Various embodiments of the dual/multiple measurement approach are shown in Figures 6B-F. As shown in Figure 6B, waveguide 26 is formed with a pair of spaced parallel clad segments 28a,b each of which has a different specificity to a particular chemical species or group of chemical species. A pair of sources 22a,b and a pair of detectors 24a,b are positioned around the waveguide 26, with one of each pair aligned with one of the clad segments 28a,b. By using highly directional sources 22a,b, or by using additional optics, the light beam from source 22a to detector 24a will be affected by clad segment 28a but not significantly by clad segment 28b, and light from source 22b to detector 24b will be affected only by clad segment 28b; i.e., the light beams from the two sources will propagate along separate channels or portions of the waveguide and each will only be affected by one clad segment. The outputs of detectors 24a,b can then be processed to provide desired information.

[0021] Alternative configurations include the use of a single source with a pair of detectors or a single detector with a pair of sources. The particular configuration will depend partly on the spectral characteristics of available sources and detectors. Using such arrangements, the effects of each of the clad segments 28a,b can be measured and the signals processed, e.g. by processing means 27 (Figure 6A) such as a digital computer, to provide desired information about particular chemical species. Of course, the principles can be generalized to more than two clad segments.

[0022] As shown in Figure 6C, a waveguide 26 with spaced parallel clad segments 28a,b is positioned between a single source 22 and detector 24. A mechanical shutter or chopper 30 is positioned between the waveguide 26 and detector 24 in order to alternately pass the signal produced by one clad segment while blocking the effect produced by the other clad segment. In the configurations of 6B and C, the clad segments should be oriented parallel to the axis between the source and detector to define somewhat separate channels wherein different effects on signal transmission can be detected, either simultaneously (Figure 6B) or alternately (Figure 6C).

[0023] However, if suitable sources and detectors are available, a more general configuration of waveguide 26 with clad segments 28a,b can be positioned between a single source 22 and single detector 24 as shown in Figure 6D. For example, dichromatic LED lamps and color sensors are available. The specificity and sensitivity of a clad segment to a chemical species can also be a function of the wavelength of the light. Thus, a light signal of two wavelengths, each of which is affected differently by the two clad segments can be input and the variation at the two frequencies can be detected. Alternatively, two sources of different wavelengths and/or two detectors can be used.

[0024] When the available sources and/or detectors do not allow simultaneous measurement of the effects produced by two different clad segments, it may be possible to perform sequential measurements of these effects. For example, as shown in Figure 6E, the waveguide 26 with clad segments 28a,b is positioned between a source 22 and detector 24. Sample from reservoir 32 is flowed through a control valve 36 into a pair of flow channels 34a,b which contact clad segments 28a,b, respectively. The sample can first be flowed through channel 34a to produce a response due to clad segment 28a and then flowed through channel 34b to produce a response due to clad segment 28b.

[0025] In addition to measuring the light transmitted through the waveguide, it is also possible to measure the light lost through the clad segment. For example, in Figure 6F a waveguide has a plurality of circular clad segments 28a,b,c,d and is positioned between a source 22 and detector 24a. Fiber optic or other suitable detectors 38a,b,c,d are positioned to measure the light leakage through clad segments 28a,b,c,d, respectively. The signals from light sensors 38a,b,c,d pass through a multiplexer 40 into a second detector 24b so that the light leakage signals can be measured.

[0026] The ability to accurately measure the intensity changes caused by leakage through the clad segment is important. As shown in Figure 7, a waveguide structure 12/14 with clad segment 18 is positioned between a source 22

and detector 24. Light from the source 22 which enters waveguide body 12 through end face 16 and is incident on clad 14 at an angle less than the critical angle defined by the refractive index ratio will be totally internally reflected as illustrated. However, some light will propagate substantially down the center of the waveguide; this is particularly so when source 22 is not highly directional. This unreflected light passes straight down the waveguide and provides a large background signal at detector 24. To reduce or eliminate this problem, detector masking means 42 can be positioned on detector 24 and/or detector masking means 44 can be positioned on end face 16 to substantially block the unreflected background light which passes straight down the center of the waveguide while permitting substantially all the totally internally reflected light to reach the detector.

[0027] The refractive index and sensitivity of the clad segment are important parameters of the waveguide sensor. However, in some circumstances the available materials may not provide the desired values. One approach, as illustrated in Figure 8 is to form clad segment 18 of two different materials, e.g. a thin metal layer 46 overcoated by a polymer layer 48, or vice-versa, which together produce the desired properties. For example, metal layer 46 can be chosen for its affinity to the species and polymer 48 (which is permeable to the species) can provide the desired refractive index N3 of clad segment 18 (N3 will be determined by index N5 of layer 46 and index N6 of layer 48). The refractive index of select metals, at various wavelengths, are listed in Table 1 and the refractive index of select polymers is shown in Table 6. Combinations of these can be used as described.

[0028] A further possibility to provide selectivity of the clad segment where a suitable material is not available, but a good material is available which is specific to a reaction product of the species, is to include a catalyst in the clad segment. Clad segment 18 can include a catalyst embedded or dispersed therein, or a separate catalyst layer can be applied on the species-specific clad layer, e.g. in Figure 8, layer 46 is the specific clad material and layer 48 is the catalyst. The catalyst will catalyze a reaction of the species of interest to form a reaction product to which the clad segment has strong affinity. As an example, TCE could be detected by a waveguide sensor having a clad segment specific to HCl and a catalyst to react with the TCE to form HCl.

[0029] The specificity or affinity of the clad has been further defined in terms of various parameters, particularly surface structure as well as crystallographic orientation. A methodology for tailoring a waveguide sensor to a particular chemical species by appropriate choice of the refractive indexes is provided. Multiple clad segments are used to identify a particular species from a group of species which interact with some clad materials. A clad segment of two different materials, one to provide refractive index and the other to provide species selectivity, can be used, as well as a clad segment with a catalyst to react the species of interest to provide a reaction product for which the clad segment has a strong affinity.

[0030] The substrate is usually glass or quartz. This material has a refractive index of 1.47(6) at 400 nm, 1.46(2) at 500 nm and 1.45(7) at 650 nm. Special substrates can be made of a variety of materials, e.g., NaCl, N=1.54(4); AgCl, N=2.07(1); Ag₂SO₄, N=1.75(8); MgF₂, N=1.378; Li₂SO₄, N=1.46(5), and Al₂(SO₄)₃, N=1.47. In fact, any material which can be made into a plate which can propagate light is a possible substrate.

[0031] In the waveguide structures according to the invention, the clad segments are typically about a monolayer to about 50 Å thick. The waveguide body must have sufficient rigidity so that the light propagation pattern is not affected by flexing.

[0032] These thin metal clads can be chosen with an effective light porosity or transmissivity when in contact with a species of interest to change the light transmission through the waveguide as a function of the refractive index of the chemical species of interest present in the surrounding medium. The light porosity of the clad is a function of the clad material, its thickness and its physical characteristics such as physical porosity and crystalline structure. The metal clad is selected of a suitable thickness to produce a gradient refractive index at the interface between the waveguide body and the clad segment as a result of chemical species of interest from the surrounding medium being absorbed on the metal clad. This localized refractive index at the boundary between the waveguide body and clad segment is directly proportional to the amount of the chemical species adsorbed/absorbed on the clad segment and also its refractive index. The amount of light leaking from the waveguide through the clad depends on the amount and refractive index of the chemical species. The light leakage substantially modulates the light signal transmitted through the core, producing a detectable measure of the presence of the chemical species and its refractive index.

[0033] The metal coatings are key to the selection process. They are selected both because they have specific affinity to various species and because they have appropriate refractive indexes. The index of refraction of several metals, for several wavelengths, are given in Table 1.

TABLE 1

Wavelength (nm)	Photon Energy (ev)	Refractive Index			
		(Cr)	(Ni)	(Rh)	(Pt)
990	1.25	4.50	2.91	3.39	3.42
660	1.88	3.66	2.10	2.22	2.48
550	2.26	3.31	1.78	1.98	2.13
480	2.59	2.22	1.65	1.85	1.92

[0034] The affinity depends on the metal selected, the thickness of the coating and the method of attachment. The crystal structure and orientation is very important in the selectivity process. Furthermore, the more ordered the crystal, the better it behaves as a sensing material, e.g., Ni(111) and Ir(110) both absorb benzene, but the Ni(111) is ordered while the Ir(110) is disordered and the Ni(111) performs much better. The type of absorption, i.e., mechanical, chemical, electrostatic, solvation, etc. also determines the effectiveness of the metal coating.

[0035] The metal claddings that may be utilized as the clad segments on the waveguide include:

- 1) group IVB elements: Titanium (Ti), Zirconium (Zr), Hafnium (Hf);
- 2) group VB elements: Vanadium (V), Niobium (Nb), Tantalum (Ta);
- 3) group VIB elements: Chromium (Cr), Molybdenum (Mo), Tungsten (W);
- 4) group IB elements: Copper (Cu), Silver (Ag), Gold (Au);
- 5) group IIB elements: Zinc (Zn), Cadmium (Cd);
- 6) group VIII elements: Iron (Fe), Ruthenium (Ru), Cobalt (Co), Rhodium (Rh), Nickel (Ni), Palladium (Pd), Platinum (Pt), Iridium (Ir), Osmium (Os);
- 7) Oxides of the above metals;
- 8) Metal compounds or alloys such as:
 - a) group II-VI compounds: including but not limited to ZnSe, ZnTe, CdS, CdTe, MgTe, ZnS;
 - b) group III-V compounds: including but not limited to BN, GaAs, InAs, InSb, AlN, GaN, InN;
 - c) group I-VII compounds: including but not limited to CuCl, CuBr, AgI;
 - d) sphalerite structure compounds: including but not limited to Ga₂Te₃, ZnSnP₂, ZnSnAs₂;
 - e) Wurtzite structure compounds: including but not limited to SiC, MnS, MnSe, MnTe, Al₂Se₃;
 - f) group I, III, VI compounds: including but not limited to CuGaTe₂, CuGaSe₂, CuLaS₂;
 - g) group II, IV, V compounds: including but not limited to ZnGeP₂, CdGeP₂, ZnGeAs₂, ZnSnAs₂.

[0036] The metal coatings can be deposited on the waveguide surface by sputtering, brush coating, vacuum deposition, plasma coating, or by any other technique that can form either a homogeneously- or heterogeneously-coated surface. Various lithographic techniques can be used to produce the appropriate clad segment patterns. Either inorganic or organometallic compounds can be used to deposit metal coatings on the waveguide. The metals can also be deposited from their elemental states. The final coating deposited on the waveguide can be in the form of either elemental metal or any of its oxides or other metal compounds or alloys.

[0037] The clad segments are made of materials which have a strong affinity for the chemical species of interest. The affinity is determined by a number of different factors such as chemical or mechanical adsorption, pore size, electrostatic attraction, or ability to dissolve the species. The affinity of the clad segment for the species is illustrated in Figure 3C in which atoms or molecules 17 of the species are adsorbed in pores 19 (indicated by cell structure) formed in clad segment 18.

[0038] The metal clads show varying sensitivities or selectivities for different chemical species. The variation of sensor response to various chemical species is illustrated in Table 2 where V_0 is the detector voltage output in the absence of the chemical species (i.e., no light leakage) and V is the detector output voltage in the presence of a given amount of the chemical species. Certain metals are particularly sensitive to certain chemical species while relatively insensitive to others. Each chemical species can be detected by a number of different metal clads.

TABLE 2

Ru	V ₀	V
Gasoline	7.27	3.87
Benzene	7.00	4.19
Xylene	7.38	4.39
Toluene	7.07	4.10
V		
Gasoline	6.85	5.80
Benzene	5.32	3.79
Zr		
Gasoline	8.20	5.89
Benzene	8.00	2.28
Xylene	7.68	3.62
Toluene	7.51	4.57
Ni		
Gasoline	9.46	6.74
Benzene	7.48	1.07
Xylene	8.56	1.27
Toluene	8.16	1.77
Pd		
Gasoline	7.51	4.92
Benzene	8.00	6.78
Xylene	7.44	5.00
Fe		
Benzene	8.96	1.65

[0039] Table 3 lists a number of illustrative metal surfaces and various gases which have been found to be adsorbed on the metal surface. The adsorbability of the gases may depend on the crystal form and/or orientation of the metal layer. In the process of forming the metal clad segment on the waveguide, particular crystal forms of the metal can be reproducibly obtained by controlling the process parameters, e.g. temperature and pressure, so that a sensor tailored to a specific gas can be obtained. Thus, a sensor with a metal clad segment of preselected crystal structure can be produced for use with a desired analyte. Table 4 similarly lists a number of illustrative metal surfaces and various organic compounds (hydrocarbons) which have been found to be adsorbed on the metal surface. Certain metals, and in some cases certain crystal forms of some metals, are thus particularly suitable for the metal clad segment for detection of certain hydrocarbons. The lists of Tables 3 and 4 are only for purposes of illustration and are not exhaustive of all possible combinations. Further information about adsorption of gases by metal surfaces is contained in Chemistry In Two-Dimensional Surfaces, Garbor A. Somorjai, Cornell Univ. Press, Ithaca, NY, 1981, particularly Tables 5.2-5.7, pp. 210-241, which are herein incorporated by reference.

TABLE 3

SURFACE		ADSORBED GAS
A1	(111), (100), (110)	O ₂

TABLE 3 (continued)

SURFACE		ADSORBED GAS
Au	(111)	O ₂
	(100)	H ₂ S, CO, Xe
Cu	(111)	O ₂ , CO, Cl ₂ , H ₂ S, Xe
	(100)	O ₂ , CO, N ₂
Cu/Ni	(110)	O ₂ , CO, H ₂ O, H ₂ S, Xe
	(111)	CO
Fe	(110)	O ₂ , CO, H ₂ S
	(111)	O ₂ , NH ₃ , H ₂
Fe/Cr	(100)	O ₂ , CO, H ₂ S, H ₂ , NH ₃ , H ₂ O
	(110)	O ₂ , CO, N ₂ , H ₂ , H ₂ S
Mo	(100), (110)	O ₂
Ni	(111)	O ₂ , H ₂ S
	(100)	O ₂ , CO, H ₂ , N ₂ , H ₂ S
NiO	(110)	O ₂ , CO, CO ₂ , H ₂ , N ₂ , H ₂ S
	(111)	O ₂ , CO, CO ₂ , H ₂ , NO, H ₂ S, H ₂ Se, Cl ₂
Pt	(100)	O ₂ , CO, CO ₂ , H ₂ , H ₂ S, Te, Xe
	(110)	O ₂ , CO, H ₂ , NO, H ₂ O, H ₂ S, H ₂ Se
Rh	(101)	H ₂ , H ₂ S, Cl ₂
	(111)	O ₂ , CO, H ₂ , NO, H ₂ O, S ₂ , N
Zn ZnO	(100)	O ₂ , CO, H ₂ , NO, N, H ₂ S, S ₂
	(110)	O ₂ , CO, C ₃ O ₂ , NO, H ₂ S
Zn ZnO	(111), (100)	O ₂ , CO, CO ₂ , H ₂ , NO
	(110)	O ₂ , CO
Zn ZnO	(0001)	O ₂
	(1010)	O ₂

TABLE 4

SURFACE		ADSORBED GAS
Fe	(100)	C ₂ H ₄
Ir	(111)	C ₂ H ₂ , C ₂ H ₄ , cyclohexane, benzene
	(100)	C ₂ H ₂ , C ₂ H ₄ , benzene
Mo	(110)	C ₂ H ₄ , benzene
	(100)	CH ₄
Ni	(111)	CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , cyclohexane, benzene
	(100)	CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , benzene
	(110)	CH ₄ , C ₂ H ₄ , C ₂ H ₆ , C ₅ H ₁₂

TABLE 4 (continued)

SURFACE		ADSORBED GAS
Pt	(111)	C ₂ H ₂ , C ₂ H ₄ , <i>n</i> -butane, <i>n</i> -pentane, <i>n</i> -hexane, <i>n</i> -heptane, <i>n</i> -octane, cyclohexane, benzene, toluene, naphthalene, pyridine, <i>m</i> -xylene, mesitylene, <i>T</i> -butylbenzene, <i>N</i> -butylbenzene, aniline, nitrobenzene, cyanobenzene
	(100)	C ₂ H ₂ , C ₂ H ₄ , benzene, naphthalene, pyridine, toluene, <i>M</i> -xylene, mesitylene, <i>T</i> -butylbenzene, <i>N</i> -butylbenzene, aniline, nitrobenzene, cyanobenzene, C ₂ N ₂
	(110)	HCN, C ₂ N ₂
Rh	(111),(100),(331)	C ₂ H ₂ , C ₂ H ₄

[0040] The specificity of different metal clads to various analytes allows more specific analysis of an analyte mixed with other substances. The invention further includes multiple measurement methods and apparatus. Since more than one clad may be available for a particular analyte, but each clad will not have the same absorption coefficients to other analytes, a more complex measurement method and sensor structure can be used to determine the presence of a selected analyte out of a mixture of several different analytes. To detect analyte A in a mixture of analytes A and B, it would be most desirable to find a single metal surface that is specific to A. However, if one cannot be found, two sensors can be used, one which has a clad which responds to both A and B and one which has a clad which responds to B but not A. By subtracting the measurement obtained from the second sensor from that of the first sensor, a measure of analyte A is obtained.

[0041] Alternatively, if a specific metal clad is not available for either A or B, then clads are chosen which have different absorption coefficients for A and B, and the concentration of A and B are obtained by solving an algorithm for two unknowns. The dual sensor approach can be extended to multiple sensors for more than two analytes and can be implemented in a variety of ways, using either a single waveguide or multiple waveguides.

[0042] The crystallographic orientation of the metal coatings is particularly important since the affinity of various chemical species is often strongly dependent on the crystallographic form of the metal. The planar waveguide is a highly advantageous structure for depositing clad segments having preferred crystallographic orientations, since deposition on a flat surface is much easier to perform using known deposition techniques.

[0043] In accordance with the invention, and as shown in Table 5, pairs of clad segments, each responsive to different combinations of different chemical species, can be used to detect a particular species by subtracting one response from another when a particular clad which responds directly to a single species is not available.

TABLE 5

Be (0001)	O ₂ ,	CO,	H ₂ ,	N ₂		
Cu (100)	O ₂ ,	CO,		N ₂		
[Be(0001)] - [Cu (100)]			H ₂			
Mo (100)	O ₂ ,	CO,	H ₂ ,	N ₂ ,	H ₂ S	
Be (0001)	O ₂ ,	CO,	H ₂ ,	N ₂		
[Mo (100)] - [Be (0001)]					H ₂ S	
Co (100)	CO,	O ₂				
Cr (100)		O ₂				
[Co (100)] - [Cr (100)]			CO			
Mo (110)	O ₂ ,	CO,	CO ₂ ,	H ₂ ,	N ₂ ,	H ₂ S
Mo (100)	O ₂ ,	CO,		H ₂ ,	N ₂ ,	H ₂ S
[Mo (110)] - [Mo (100)]			CO ₂			
Ru (101)	O ₂ ,	CO,	NO			
Co (100)	O ₂ ,	CO				
[Ru (101)] - [Co (100)]			NO			

[0044] In addition to the crystallographic orientation of the surface, the surface structure itself provides specificity. For example, Pt(111) adsorbs *n*-butane, *n*-pentane, *n*-hexane, and *n*-octane. If the surface structures are considered, preference can be attained. The preferred structures of the Pt(111) surface for these species are:

$$\begin{array}{ll}
 \textit{n-butane} & \begin{pmatrix} 2 & 1 \\ -1 & 2 \end{pmatrix} \\
 \textit{n-pentane} & \begin{pmatrix} 2 & 1 \\ 0 & 6 \end{pmatrix} \\
 \textit{n-hexane} & \begin{pmatrix} 2 & 1 \\ 0 & 8 \end{pmatrix} \\
 \textit{n-octane} & \begin{pmatrix} 2 & 1 \\ -1 & 4 \end{pmatrix}
 \end{array}$$

[0045] For these linear molecules, therefore,

$$\begin{pmatrix} 2 & 1 \\ x & y \end{pmatrix}$$

is the general surface structure. It is important to note that for cyclohexane, this changes and the surface structure becomes

$$\begin{pmatrix} 4 & -1 \\ 1 & 5 \end{pmatrix} .$$

[0046] Therefore, according to the invention, by forming clad segments of particular materials, with particular crystallographic orientations and specific surface structures, specificity for individual species can be better achieved.

[0047] The Pt(111) example illustrates the use of different surface structures of a material to select between closely related compounds with very similar chemical structures. The ability to distinguish between compounds with very similar chemical structures, without doing a detailed spectral analysis, is very important to sensor technology. The same approach is applicable to separate benzene, toluene, and xylene.

[0048] Whereas the surface structures give good species separation, improvements can be made on specificity by further focusing on refractive index differences. This can be accomplished in two (2) ways: (i) undercoating or overcoating the metal film; and (ii) adjusting the refractive index of the substrate (N1) by selecting a suitable material for the substrate.

[0049] The overcoating (or undercoating) of the metal film will, among other materials, be a polymer. These materials, nominally, have refractive indexes between 1.34 and 1.64. Examples of these are given in Table 6.

TABLE 6

Compound	Refractive Index
Poly(tetrafluoroethylene-co-hexafluoropropylene)	1.338
Poly(pentafluoropropyl acrylate)	1.385
Poly(butyl acrylate)	1.466
Poly(n-butyl methacrylate)	1.481

TABLE 6 (continued)

Compound	Refractive Index
Cellulose Nitrate	1.500
Poly (N-benzyl methacrylamide)	1.596

[0050] It is possible to find metal surfaces which will selectively adsorb target compounds. This can range from a single species to a group of compounds. These surfaces are anything but perfect when it comes to completely isolating a particular target and secondary species sorting may help. As an example, in environmental analysis, separation and analysis of the organic chlorides is an important task. Typical compounds are chloroform [$N = 1.448(6)$], trichloroethylene (TCE) [$N = 1.477(5)$], and the chlorophenols [$N_{2\text{-chloro}} = 1.557(9)$, $N_{3\text{-chloro}} = 1.556(5)$, $N_{4\text{-chloro}} = 1.541(9)$]. The metal is chosen to selectively adsorb the organic chlorides while an overcoating (or undercoating) is used to control light leakage. For the above compounds, if the overcoating has $1.448 < N < 1.477$ (e.g., cellulose acetate butyrate) only the chloroform controls the light. As shown in Table 7, proper selection of overcoating makes species concentrations available by difference.

TABLE 7

Species	Compound	Nc	Typical Overcoat	No	Measured Species
1	Chloroform	1.448	cellulose acetate butyrate	1.460	1
2	TCE	1.477	Poly(n-butyl methacrylate)	1.480	1+2
3	4-chlorophenol	1.541	Poly(N-allyl methacrylate)	1.547	1+2+3
4	3-chlorophenol	1.556	Epoxy Resin	1.557	1+2+3+4
5	2-chlorophenol	1.557	Poly(benzyl methacrylate)	1.568	1+2+3+4+5

[0051] For example, to obtain inputs on 3-chlorophenol (species 4) subtract 3 from 4, i.e., $[(1+2+3+4) - (1+2+3) = 4]$.

[0052] Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended claims.

Claims

1. A waveguide sensor (10) for measuring refractive index and identifying chemical species of a surrounding medium, comprising:

an optical waveguide body (12) having a refractive index N_1 ;

a clad (14) including a thin film metal clad segment (18) of metal or metal oxide or other metal compound or alloy formed on the surface of the waveguide body (12), the metal clad segment (18) having a refractive index N_3 , and an effective thickness and light transmissivity which in combination with the surrounding medium produces a localized refractive index N^* such as to cause a controlled leakage of light from the waveguide body (12) which modulates the transmission of light through the optical waveguide body (12) as a function of the refractive index of the surrounding medium, the remainder of the clad (14) having a refractive index N_2 less than N_1 ;

a light source (22) operatively associated with the optical waveguide body (12) for inputting a light signal into the optical waveguide body (12);

detection means (24) operatively associated with the optical waveguide body to detect signals produced by said modulation; and

processing means for calculating information about a particular compound of interest from the signals produced by said modulation;

characterised in that the optical waveguide body (12) is planar, having a flat surface bearing the clad as a patterned coating thereon; the clad having a plurality of metal clad segments (28a, 28b...), each having different selectivity to chemical species of interest, including a pair of metal clad segments (18, 28a...) selected from:

a) Be (0001) and Cu (100);

b) Mo (100) and Be (0001);

- c) Co (100) and Cr (100);
- d) Mo (110) and Mo (100);
- e) Ru (101) and Co (100); and

5 in that the detection means comprises means for detecting a signal produced by each of the pair of metal clad segments and the processing means comprises means for subtracting the signals produced by the pair of metal clad segments from one another.

10 2. The sensor of Claim 1 further comprising an overlayer or underlayer (46, 48) of a second material on the metal clad segment, the metal clad segment having a strong affinity for a chemical species of interest, the second material having a suitable refractive index to produce controlled light leakage in the presence of the chemical species.

3. The sensor of Claim 2 wherein the second material is a polymer with a refractive index in the range or about 1.34 to about 1.64.

15 4. The sensor of Claim 3 wherein the polymer is selected from poly(tetrafluoroethylene-cohexafluoropropylene), poly(pentafluoropropyl acrylate), poly(butyl acrylate), poly(n-butyl methacrylate), cellulose nitrate, and poly(N-benzyl methacrylamide).

20 5. The sensor of Claims 1 to 4 further comprising a catalyst on the metal clad segment for reacting with the species of interest to form a reaction product, wherein the metal clad segment is specific to the reaction product.

6. The sensor of Claims 1 to 5 wherein the optical waveguide body (12) is formed of SiO₂ (glass/quartz), NaCl, AgCl, Ag₂SO₄, MgF₂, Li₂SO₄, or Al₂(SO₄)₃.

25 7. A method of detecting the refractive index and identifying chemical species of a medium, comprising:

30 providing a waveguide sensor (10) according to claim 1;
contacting the thin film metal clad segments (18) with the medium;
inputting a light signal from said source (22) into the optical waveguide body (12);
detecting the signals produced by each of the pair of metal clad segments;
and subtracting the signals from one other.

35 8. The method of Claim 7 further comprising forming an overlayer or underlayer (46, 48) of a second material on the metal clad segment, the metal clad segment having a strong affinity for a chemical species of interest, the second material having a suitable refractive index to produce controlled light leakage in the presence of the chemical species.

40 9. The method of Claim 7 or 8 further comprising adding a catalyst to the metal clad segment for reacting the species of interest to form a reaction product and forming the metal clad segment specific to the reaction product.

10. A method of forming a refractive index waveguide sensor comprising:

45 providing an optical waveguide body (12) having a refractive index N₁; forming a clad on the optical waveguide body;
the clad (14) including a thin film metal clad segment (18) of metal or metal oxide or other metal compound or alloy formed on the surface of the waveguide body (12), the metal clad segment (18) having a refractive index N₃, and an effective thickness and light transmissivity which in combination with the surrounding medium produces a localized refractive index N* such as to cause a controlled leakage of light from the waveguide body
50 (12) which modulates the transmission of light through the optical waveguide body (12) as a function of the refractive index of the surrounding medium, the remainder of the clad (14) having a refractive index N₂ less than N₁;
providing a light source (22) operatively associated with the optical waveguide body (12) for inputting a light signal into the optical waveguide body (12);
55 providing detection means (24) operatively associated with the optical waveguide body to detect signals produced by said modulation; and
providing processing means for calculating information about a particular compound of interest from the signals produced by said modulation;

characterised in that the optical waveguide body (12) is planar, having a flat surface bearing the clad as a patterned coating thereon; the clad having a plurality of metal clad segments (28a, 28b...), each having different selectivity to chemical species or interest, including a pair of metal clad segments (18, 28a...) selected from:

- a) Be (0001) and Cu (100);
- b) Mo (100) and Be (0001);
- c) Co (100) and Cr (100);
- d) Mo (110) and Mo (100);
- e) Ru (101) and Co (100); and

in that the detection means comprises means for detecting a signal produced by each of the pair or metal clad segments and the processing means comprises means for subtracting the signals produced by the pair of metal clad segments from one another.

11. The method of Claim wherein the step of forming the metal clad segment (18) on the portion of the optical waveguide body is performed by sputtering, vacuum deposition, plasma coating, brush coating, or spin coating of said metal.

12. The method of Claim 10 or 11 further comprising applying an over/underlayer (46, 48) of a second material on the metal clad segment (18), the metal clad segment (18) having a strong affinity for a chemical species of interest, the second material having a suitable refractive index to produce controlled light leakage in the presence of the chemical species.

13. The method of Claims 10 to 12 further comprising applying a catalyst on the metal clad segment (18) for reacting with a species of interest to form a reaction product, wherein the metal clad segment (18) is specific to the reaction product.

14. The sensor according to claim 1 comprising alternative viewing means positioned between the optical waveguide body and detection means for alternatively passing a light beam affected by one of the clad segments while blocking a light beam affected by the other clad segment.

15. The sensor according to claim 1 further comprising means for alternately flowing a sample over one of the metal clad segments while preventing flow over the other metal clad segments.

16. The sensor according to claim 1 further comprising light blocking means positioned on at least one of the optical waveguide body detection means for substantially blocking background light passing straight down the center of the optical waveguide body from reaching the detection means.

Patentansprüche

1. Wellenleiter-Sensor (10) zum Messen des Brechungsindex und zum Identifizieren der chemischen Spezies eines umgebenden Mediums, mit

- einem Wellenleiter-Körper (12) mit einem Brechungsindex N_1 ;
- einer Kaschierung (14), die ein dünnsschichtiges metallkaschiertes Segment (18) aus Metall oder Metalloxid oder einer anderen Metallverbindung oder Legierung aufweist, die auf der Oberfläche des Wellenleiter-Körpers (12) ausgebildet ist, wobei das metallkaschierte Segment (18) einen Brechungsindex N_3 sowie eine effektive Dicke und ein Licht-Transmissionsverhalten aufweist, was in Kombination mit dem umgebenden Medium einen örtlichen Brechungsindex N^* erzeugt derart, dass aus dem Wellenleiter-Körper (12) ein kontrollierter Austritt von Licht erfolgt, der den Durchgang von Licht durch den optischen Wellenleiter-Körper (12) als Funktion des Brechungsindex des umgebenden Mediums moduliert, wobei die restliche Kaschierung (14) einen Brechungsindex N_2 hat, der kleiner als N_1 ist;
- einer Lichtquelle (22), die betrieblich dem optischen Wellenleiter-Körper (12) zugeordnet ist, um ein Lichtsignal in diesen einzuspeisen;
- einer Detektoreinrichtung (24), die betrieblich dem optischen Wellenleiter-Körper zugeordnet ist, um durch die Modulation erzeugte Signale zu erfassen;
- und mit einer Verarbeitungseinrichtung, um aus den durch die Modulation erzeugten Signalen Informationen über eine bestimmte interessierende Verbindung zu berechnen,

dadurch gekennzeichnet, dass der optische Wellenleiter-Körper (12) ebenflächig ist und eine flache Oberfläche aufweist, die die Kaschierung als gemusterten Belag trägt, wobei die Kaschierung eine Vielzahl von metallkaschierten Segmenten (28a, 28b ...) jeweils mit einer anderen Selektivität für die interessierenden chemischen Spezies aufweist und die Kaschierung ein Paar metallkaschierter Segmente (18, 28a ...) einschließt, die aus

- a) Be (0001) und Cu (100),
- b) Mo (100) und Be (0001),
- c) Co (100) und Cr (100),
- d) Mo (110) und Mo (100) und
- e) Ru (101) und Co (100)

ausgewählt sind,

dass die Detektoreinrichtung eine Einrichtung aufweist, mit der ein von jedem Segment des Paares metallkaschierter Segmente erzeugtes Signal erfassbar ist, und dass die Verarbeitungseinrichtung eine Einrichtung aufweist, mit der die von dem Paar metallkaschierter Segmente erzeugten Signale voneinander subtrahierbar sind.

2. Sensor nach Anspruch 1, weiterhin mit einer Über- oder einer Unterschicht (46, 48) eines zweiten Stoffes auf dem metallkaschierten Segment, wobei das metallkaschierte Segment eine hohe Affinität für eine interessierende chemische Spezies aufweist und das zweite Material einen geeigneten Brechungsindex hat, um beim Vorliegen der chemischen Spezies einen kontrollierten Lichtaustritt zu erzeugen.

3. Sensor nach Anspruch 2, bei dem das zweite Material ein Polymer mit einem Brechungsindex im Bereich von etwa 1,34 bis etwa 1,64 ist.

4. Sensor nach Anspruch 3, bei dem das Polymer gewählt ist aus der Gruppe Poly(tetrafluorethylen-co-hexafluorpropylen), Poly(pentafluorpropylacrylat), Poly(butylacrylat), Poly(n-butylmethacrylat), Cellulosenitrat und Poly(N-benzylmethacrylamid).

5. Sensor nach Anspruch 1 bis 4, weiterhin mit einem Katalysator auf dem metallkaschierten Segment zur Reaktion mit der interessierenden Spezies unter Bildung eines Reaktionsprodukts, wobei das metallkaschierte Segment für das Reaktionsprodukt spezifisch ist.

6. Sensor nach Anspruch 1 bis 5, bei dem der optische Wellenleiter-Körper (12) aus SiO_2 (Glas/Quarz), NaCl, AgCl, Ag_2SO_4 , MgF_2 , Li_2SO_4 oder $\text{Al}_2(\text{SO}_4)_3$ gebildet ist.

7. Verfahren zum Ermitteln des Brechungsindex und zum Identifizieren der chemischen Spezies eines Mediums nach Anspruch 1, bei dem man

- einen optischen Wellenleiter-Sensor (10) bereitstellt,
- die mit einer dünnen Metallschicht kaschierten Segmente (18) mit dem Medium kontaktiert;
- ein Lichtsignal aus der Quelle (22) in den optischen Wellenleiter-Körper (12) einspeist;
- die von jedem Segment des Paares metallkaschierter Segmente erzeugten Signale detektiert; und
- die Signale voneinander subtrahiert.

8. Verfahren nach Anspruch 7, bei dem man weiterhin eine Über- oder eine Unterschicht (46, 48) eines zweiten Materials auf dem metallkaschierten Segment ausbildet, wobei das metallkaschierte Segment eine hohe Affinität für eine interessierende chemische Spezies aufweist und das zweite Material einen Brechungsindex hat, der geeignet ist, um bei Vorliegen der chemischen Spezies einen kontrollierten Lichtaustritt zu erzeugen.

9. Verfahren nach Anspruch 7 oder 8, bei dem man weiterhin dem metallkaschierten Segment einen Katalysator zu gibt, um eine Reaktion mit der interessierenden Spezies unter Bildung eines Reaktionsprodukts hervorzurufen und das metallkaschierte Segment spezifisch für das Reaktionsprodukt zu machen.

10. Verfahren zur Ausbildung eines Brechungsindex-Wellenleiter-Sensors, bei dem man

- einen optischen Wellenleiter-Körper (12) mit einem Brechungsindex n_1 bereitstellt;

- auf dem optischen Wellenleiter-Körper eine Kaschierung ausbildet;
- wobei die Kaschierung (14) ein dünnnschichtiges metallkaschiertes Segment (18) aus Metall oder Metalloxid oder einer anderen Metallverbindung oder Legierung aufweist, die auf der Oberfläche des optischen Wellenleiter-Körpers (12) ausgebildet ist, das kaschierte Segment (18) einen Brechungsindex N_3 sowie eine effektive Dicke und ein Transmissionsverhalten aufweist, was in Kombination mit dem umgebenden Medium einen örtlichen Brechungsindex N^* erzeugt derart, dass ein kontrolliertes Entweichen von Licht aus dem optischen Wellenleiter-Körper (12) erfolgt, das den Durchgang von Licht durch den optischen Wellenleiter-Körper (12) als Funktion des Brechungsindex des umgebenden Mediums moduliert, und die restliche Kaschierung (14) einen Brechungsindex N_2 hat, der kleiner als N_1 ist;
- eine Lichtquelle (22) bereitstellt, die betrieblich dem optischen Wellenleiter-Körper (12) zugeordnet ist, um ein Lichtsignal in diesen einzuspeisen;
- eine Detektoreinrichtung (24) bereitstellt, die betrieblich dem optischen Wellenleiter-Körper zugeordnet ist, um durch die Modulation erzeugte Signale zu erfassen; und
- eine Verarbeitungseinrichtung bereitstellt, um aus den durch die Modulation erzeugten Signalen Informationen über eine bestimmte interessierende Verbindung zu berechnen,

dadurch gekennzeichnet, dass der optische Wellenleiter-Körper (12) ebenflächig ist und eine flache Oberfläche aufweist, die die Kaschierung als gemusterten Belag trägt, wobei die Kaschierung eine Vielzahl von metallkaschierten Segmenten (28a, 28b ...) jeweils mit einer anderen Selektivität für die interessierenden chemischen Spezies aufweist und ein Paar metallkaschierter Segmente (18, 28a ...) einschließt, die aus

- a) Be (0001) und Cu (100),
- b) Mo (100) und Be (0001),
- c) Co (100) und Cr (100),
- d) Mo (110) und Mo (100) und
- e) Ru (101) und Co (100)

gewählt sind,

dass die Detektoreinrichtung eine Einrichtung aufweist, mit der ein von jedem Segment des Paares metallkaschierter Segmente erzeugtes Signal erfassbar ist, und dass die Verarbeitungseinrichtung eine Einrichtung aufweist, mit der die von dem Paar metallkaschierter Segmente erzeugten Signale voneinander subtrahierbar sind.

11. Verfahren nach Anspruch 10, bei dem der Schritt des Ausbildens des metallkaschierten Segments (18) auf dem Teil des optischen Wellenleiter-Körpers durch Sputtern, Aufdampfen, Plasmabeschichten oder Aufbürsten des oder Schleuderbeschichten mit dem Metall erfolgt.
12. Verfahren nach Anspruch 10 oder 11, bei dem man weiterhin eine Über-/Unterschicht (46, 48) aus einem zweiten Material auf dem metallkaschierten Segment (18) ausbildet, wobei das metallkaschierte Segment (18) eine hohe Affinität für eine interessierende chemische Spezies aufweist und der Brechungsindex des zweiten Materials geeignet ist, beim Vorliegen der chemischen Spezies einen kontrollierten Lichtaustritt zu erzeugen.
13. Verfahren nach Anspruch 10 bis 12, bei dem man weiterhin auf das metallkaschierte Segment (18) einen Katalysator zur Reaktion mit einer interessierenden Spezies unter Bildung eines Reaktionsprodukts aufbringt, wobei das metallkaschierte Segment (18) für das Reaktionsprodukt spezifisch ist.
14. Sensor nach Anspruch 1 mit einer alternativen Betrachtungseinrichtung, die zwischen dem optischen Wellenleiter-Körper und der Detektoreinrichtung angeordnet ist, um abwechselnd einen von einem der kaschierten Segmente beeinflussten Lichtstrahl durchzulassen und einen vom anderen kaschierten Segment beeinflussten Lichtstrahl zu sperren.
15. Sensor nach Anspruch 1, weiterhin mit einer Einrichtung, mit der man eine Probe abwechselnd über eines der metallkaschierten Segmente fließen lassen und ein Überfließen der anderen metallkaschierten Segmente verhindern kann.
16. Sensor nach Anspruch 1, weiterhin mit einer Lichtsperrereinrichtung, die auf mindestens einer der Detektoreinrichtungen des optischen Wellenleiter-Körpers angeordnet ist und mit der Hintergrundlicht, das die Mitte des optischen Wellenleiter-Körpers gradlinig entlang verläuft, gegen ein Erreichen der Detektoreinrichtungen im wesentlichen sperrbar ist.

Revendications

1. Capteur à guide d'onde (10) pour mesurer un indice de réfraction et identifier des espèces chimiques d'un milieu environnant, comprenant :

un corps de guide d'onde optique (12) ayant un indice de réfraction N_1 ;
 un placage (14) comprenant un segment de placage métallique en film mince (18) d'un métal ou d'un oxyde de métal ou d'un autre composé métallique ou d'un alliage formé à la surface du corps de guide d'onde (12), le segment de placage métallique (18) ayant un indice de réfraction N_3 , et une épaisseur efficace et une transmissivité de la lumière qui, en combinaison avec le milieu environnant, produisent un indice de réfraction N^* localisé de façon à entraîner une fuite régulée de la lumière depuis le corps de guide d'onde (12) qui module la transmission de la lumière à travers le corps de guide d'onde optique (12) en fonction de l'indice de réfraction du milieu environnant, le reste du placage (14) ayant un indice de réfraction N_2 inférieur à N_1 ;
 une source de lumière (22) associée de façon opérationnelle au corps de guide d'onde optique (12) pour faire entrer un signal de lumière dans le corps de guide d'onde optique (12) ;
 des moyens de détection (24) associés de façon opérationnelle au corps de guide d'onde optique pour détecter des signaux produits par ladite modulation ; et
 des moyens de traitement pour calculer l'information concernant un composé particulier intéressant à partir des signaux produits par ladite modulation ;
 caractérisé en ce que le corps de guide d'onde optique (12) est plan, ayant une surface plane portant le placage sous forme d'un revêtement dessiné sur celui-ci ; le placage ayant une pluralité de segments de placage métallique (28a, 28b, ...), ayant chacun une sélectivité différente vis-à-vis d'une espèce chimique intéressante, comprenant une paire de segments de placage métallique (18, 28a, ...) choisie parmi :

- a) Be (0001) et Cu (100) ;
- b) Mo (100) et Be (0001) ;
- c) Co (100) et Cr (100) ;
- d) Mo (110) et Mo (100) ;
- e) Ru (101) et Co (100) ; et

en ce que les moyens de détection comprennent des moyens pour détecter un signal produit par chacune des paires de segments de placage métallique et les moyens de traitement comprennent des moyens pour soustraire les signaux produits par la paire de segments de placage métallique les uns des autres.

2. Capteur selon la revendication 1, comprenant en outre une couche de dessus ou une sous-couche (46, 48) d'un deuxième matériau sur le segment de placage métallique, le segment de placage métallique ayant une forte affinité pour une espèce chimique intéressante, le deuxième matériau ayant un indice de réfraction convenable pour produire une fuite de lumière régulée en présence de l'espèce chimique.
3. Capteur selon la revendication 2, dans lequel le deuxième matériau est un polymère ayant un indice de réfraction dans la gamme d'environ 1,34 à environ 1,64.
4. Capteur selon la revendication 3, dans lequel le polymère est choisi parmi le copolymère tétrafluoroéthylène-hexafluoropropylène, le poly(acrylate de pentafluoropropyle), le poly(acrylate de butyle), le poly(méthacrylate de n-butyle), le nitrate de cellulose et le poly(N-benzylméthacrylamide).
5. Capteur selon les revendications 1 à 4, comprenant en outre un catalyseur sur le segment de placage métallique pour réagir avec l'espèce intéressante pour former un produit de réaction, où le segment de placage métallique est spécifique du produit de réaction.
6. Capteur selon les revendications 1 à 5, dans lequel le corps de guide d'onde optique (12) est formé de SiO_2 (verre/quartz), NaCl , AgI , Ag_2SO_4 , MgF_2 , Li_3SO_4 ou $\text{Al}_2(\text{SO}_4)_3$.
7. Procédé de détection de l'indice de réfraction et d'identification d'une espèce chimique d'un milieu, comprenant :
- la fourniture d'un capteur à guide d'onde (10) selon la revendication 1 ;
 la mise en contact des segments de placage métallique en film mince (18) avec le milieu ;
 l'entrée d'un signal de lumière depuis ladite source (22) dans le corps de guide d'onde optique (12) ;

la détection des signaux produits par chacune des paires de segments de placage métallique ; et
la soustraction des signaux les uns des autres.

- 5 8. Procédé selon la revendication 7, comprenant en outre la formation d'une couche de dessus ou d'une sous-couche (46, 48) d'un deuxième matériau sur le segment de placage métallique, le segment de placage métallique ayant une forte affinité pour une espèce chimique intéressante, le deuxième matériau ayant un indice de réfraction convenable pour produire une fuite de lumière régulée en présence de l'espèce chimique.
- 10 9. Procédé selon la revendication 7 ou 8, comprenant en outre l'addition d'un catalyseur sur le segment de placage métallique pour réagir avec l'espèce intéressante pour former un produit de réaction, et pour former un segment de placage métallique spécifique du produit de réaction.
10. Procédé de formation d'un capteur à guide d'onde à indice de réfraction, comprenant :
15 la fourniture d'un corps de guide d'onde optique (12) ayant un indice de réfraction N1 ; la formation d'un placage sur le corps de guide d'onde optique ;
le placage (14) comprenant un segment de placage métallique en film mince (18) d'un métal ou d'un oxyde de métal ou d'un autre composé métallique ou d'un alliage formé à la surface du corps de guide d'onde (12), le
20 segment de placage métallique (18) ayant un indice de réfraction N3, et une épaisseur efficace et une transmissivité de la lumière qui, en combinaison avec le milieu environnant, produisent un indice de réfraction N* localisé de façon à entraîner une fuite régulée de la lumière depuis le corps de guide d'onde (12) qui module la transmission de la lumière à travers le corps de guide d'onde optique (12) en fonction de l'indice de réfraction du milieu environnant, le reste du placage (14) ayant un indice de réfraction N2 inférieur à N1 ;
la fourniture d'une source de lumière (22) associée de façon opérationnelle au corps de guide d'onde optique
25 (12) pour faire entrer un signal de lumière dans le corps de guide d'onde optique (12) ;
la fourniture de moyens de détection (24) associés de façon opérationnelle au corps de guide d'onde optique pour détecter des signaux produit par ladite modulation ; et
la fourniture de moyens de traitement pour calculer l'information concernant un composé particulier intéressant à partir des signaux produits par ladite modulation ;
30 caractérisé en ce que le corps de guide d'onde optique (12) est plan, ayant une surface plane portant le placage sous forme d'un revêtement dessiné sur celui-ci ; le placage ayant une pluralité de segments de placage métallique (28a, 28b, ...), ayant chacun une sélectivité différente vis-à-vis d'une espèce chimique intéressante, comprenant une paire de segments de placage métallique (18, 28a, ...) choisie parmi :
35 a) Be (0001) et Cu (100) ;
b) Mo (100) et Be (0001) ;
c) Co (100) et Cr (100) ;
d) Mo (110) et Mo (100) ;
e) Ru (101) et Co (100) ; et
40 en ce que les moyens de détection comprennent des moyens pour détecter un signal produit par chacune des paires de segments de placage métallique et les moyens de traitement comprennent des moyens pour soustraire les signaux produits par la paire de segments de placage métallique les uns des autres.
- 45 11. Procédé selon la revendication 10, dans lequel l'étape de formation du segment de placage métallique (18) sur la partie du corps de guide d'onde optique est réalisée par pulvérisation cathodique, par dépôt sous vide, par enduction au plasma, par enduction à la brosse ou par enduction centrifuge dudit métal.
- 50 12. Procédé selon la revendication 10 ou 11, comprenant en outre l'application d'une couche de dessus/sous-couche (46, 48) d'un deuxième matériau sur le segment de placage métallique (18), le segment de placage métallique (18) ayant une forte affinité pour une espèce chimique intéressante, le deuxième matériau ayant un indice de réfraction convenable pour produire une fuite de lumière régulée en présence de l'espèce chimique.
- 55 13. Procédé selon les revendications 10 à 12, comprenant en outre l'application d'un catalyseur sur le segment de placage métallique (18) pour réagir avec l'espèce intéressante pour former un produit de réaction, où le segment de placage métallique (18) est spécifique du produit de réaction.
14. Capteur selon la revendication 1, comprenant des moyens de visualisation alternatifs placés entre le corps de

guide d'onde optique et les moyens de détection pour faire passer alternativement un faisceau lumineux affecté par l'un des segments de placage tout en arrêtant un faisceau lumineux affecté par l'autre segment de placage.

- 5 **15.** Capteur selon la revendication 1, comprenant en outre des moyens pour répandre alternativement un échantillon sur l'un des segments de placage métallique tout en empêchant l'écoulement sur les autres segments de placage métallique.
- 10 **16.** Capteur selon la revendication 1, comprenant en outre des moyens d'arrêt de la lumière placés sur au moins l'un des moyens de détection du corps de guide d'onde optique pour essentiellement empêcher la lumière de fond passant directement au centre du corps de guide d'onde optique d'atteindre les moyens de détection.

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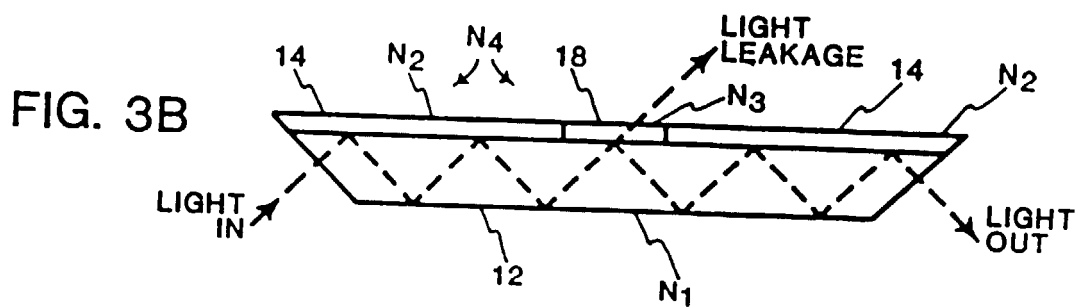
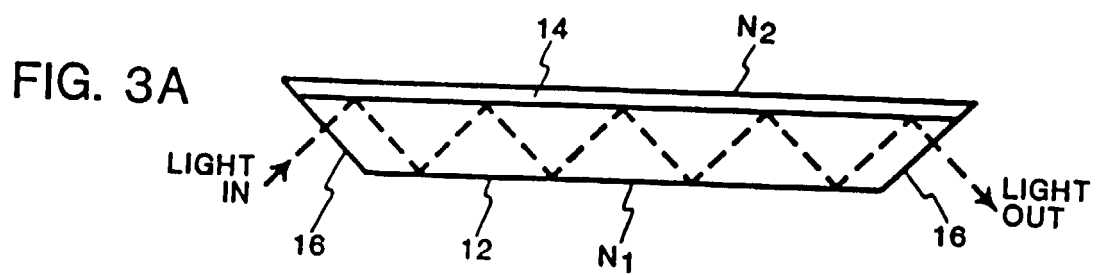
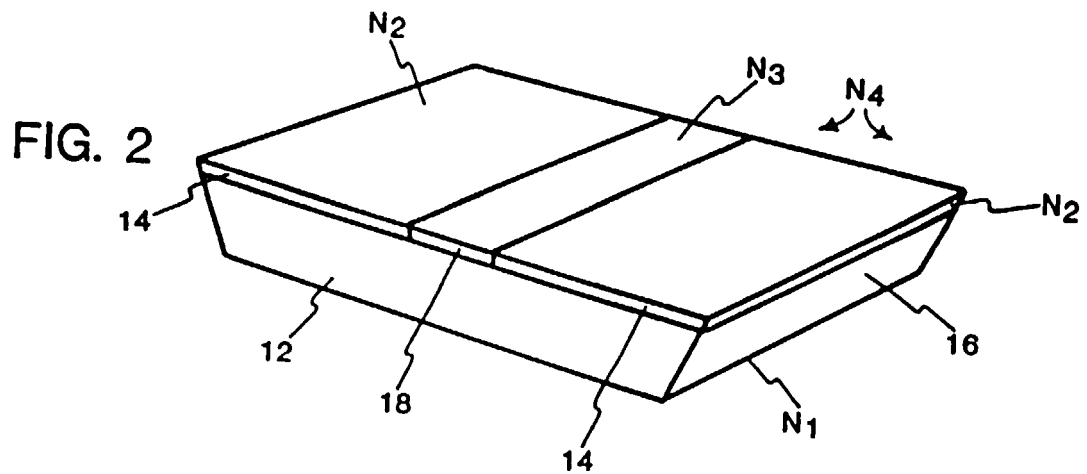
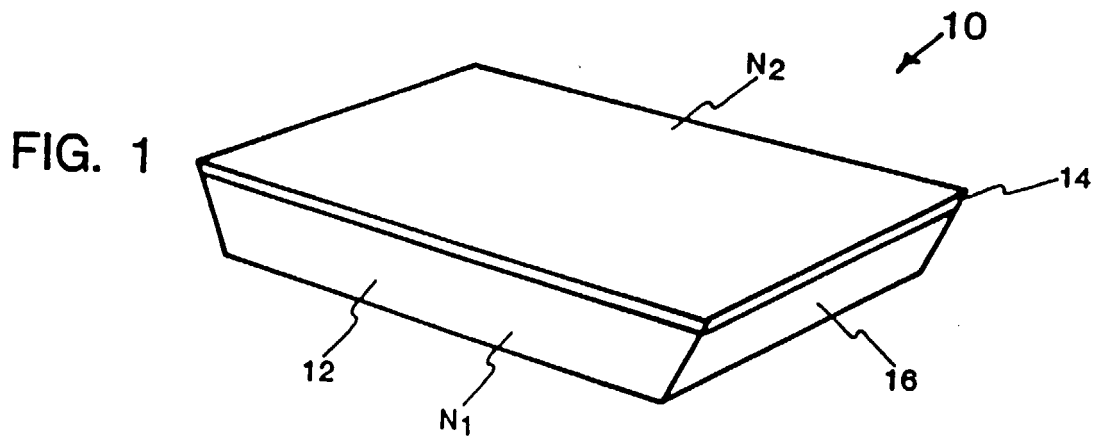


FIG. 3C

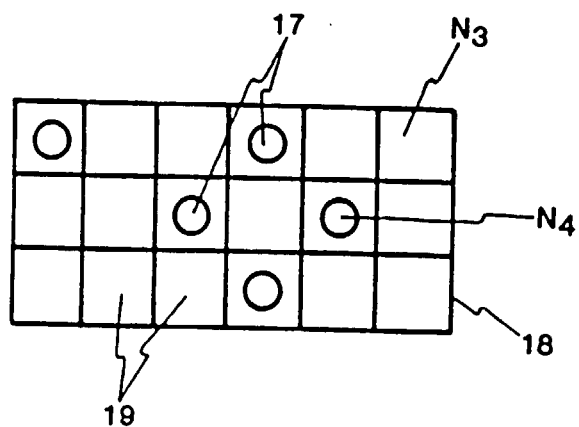


FIG. 4

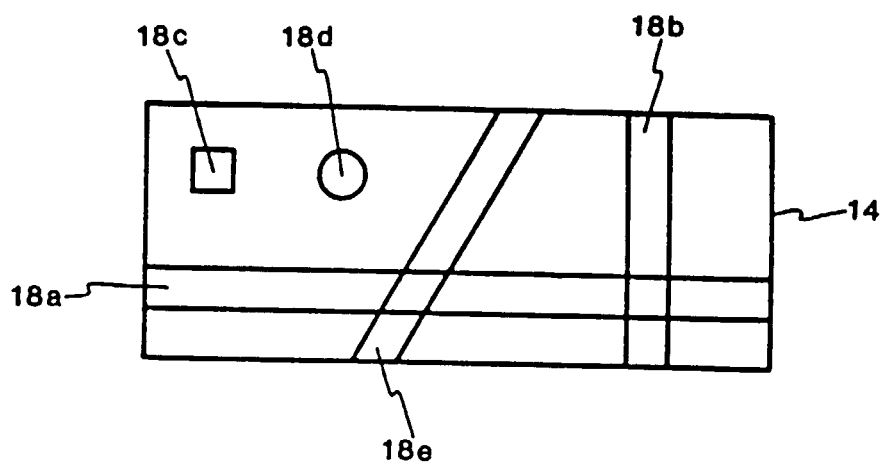
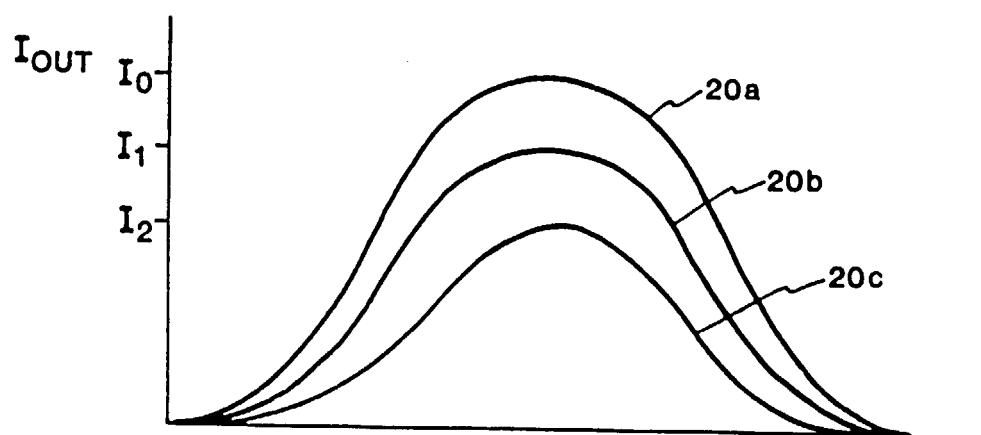


FIG. 5



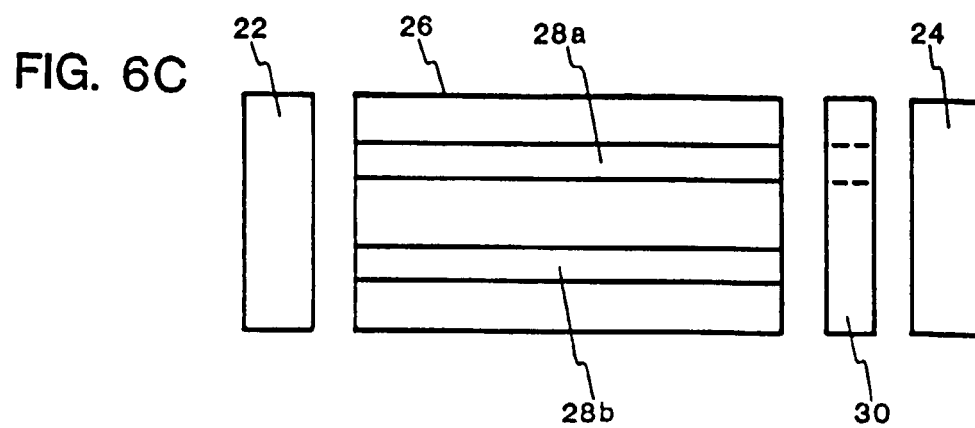
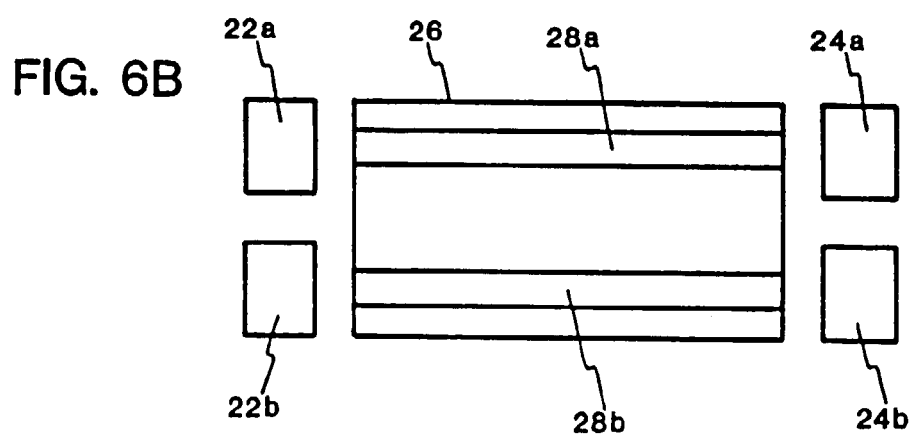
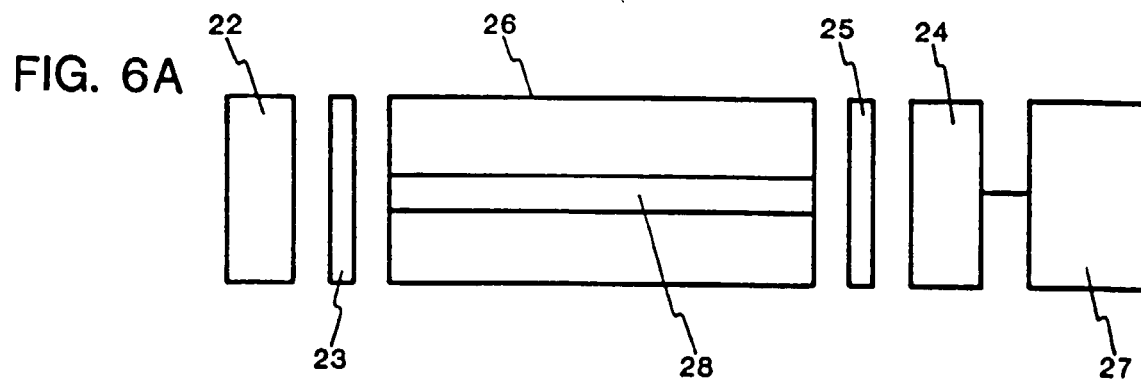


FIG. 6D

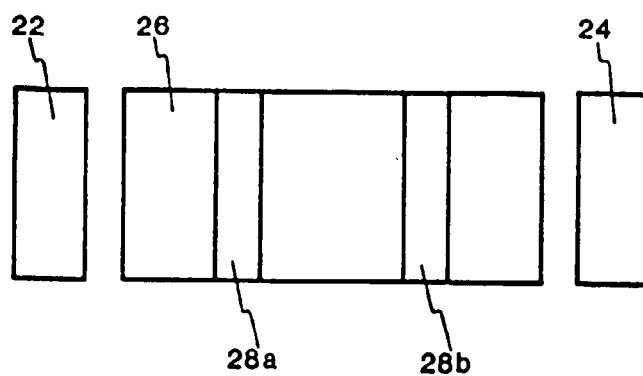


FIG. 6E

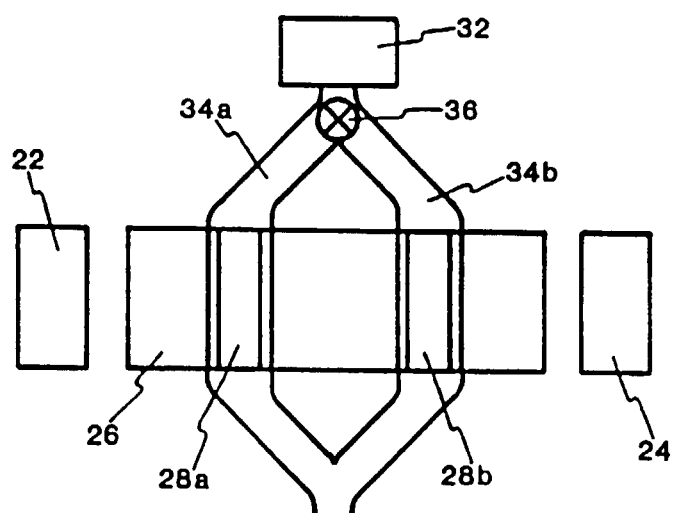


FIG. 6F

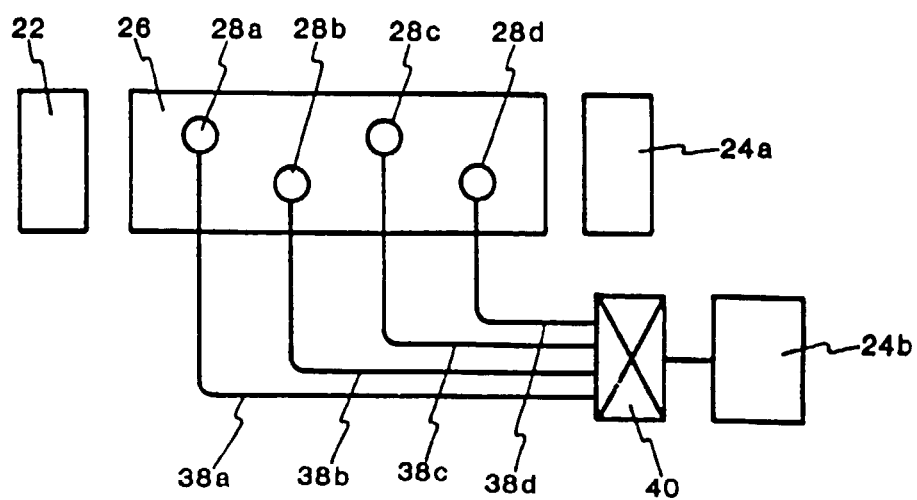


FIG. 7

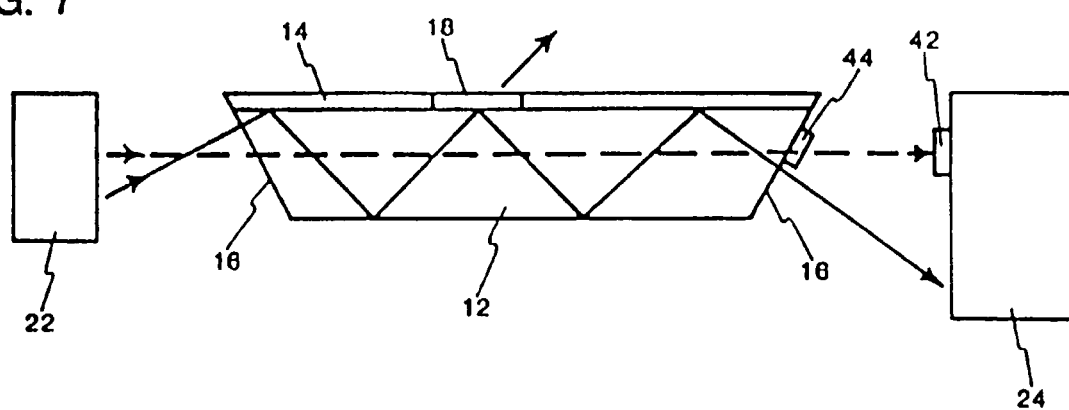


FIG. 8

